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(54) **Detergent bar composition**

(57) A detergent bar composition essentially comprising; 10 to 20% by wt. of a detergent active; 3 to 25%

by wt. of soluble alkali or alkaline earth metal sulphate
2 to 15% by wt of alkaline buffer salt 20 to 60% by wt.
of a mixture of abrasive materials.

EP 1 103 598 A1

Description**Technical Field:**

- 5 [0001] The invention relates to an abrasive detergent bar composition for cleaning hard surfaces and more particularly the compositions of the invention are suited for manual dishwashing.

Background and Prior art:

- 10 [0002] Commercial hard surface cleaning compositions typically comprise, one or more surfactants and a plurality of abrasives dispersed therein. Combinations of these together with electrolytes are generally used to form a structuring system as is well known in the art.
- [0003] Hard surfaces within household are Kitchenware, kitchen floors and platforms, floors, bathrooms etc. and one encounters different types of soil on these surfaces. The soil generally encountered on kitchenware is of two types i.e. the mobile or greasy soil and the tough or difficult to remove soil consisting of dried-on or cooked-on food. The problem becomes more pronounced when the tough soil builds on over a period of time and this requires considerable effort to clean.
- 15 [0004] Cleaning compositions in the solid form are much cheaper than liquids because of low cost packaging and these are very popular forms for developing countries. Amongst the solid form bars are gaining popularity and growing rapidly in the market of developing countries because of better value delivery. The product dosage in the solid form is easier, it avoids spillage and the product application can be better controlled. Cleaning compositions in the bar form are economically superior to other product forms and the dosage per swipe from the bar is highly controlled.
- [0005] The dish wash bars are in constant contact with water during usage and subsequent storage and hence get sogged and generally get disintegrated to paste form. Any attempt to harden the bar if not properly controlled through formulation can result into a hard product, which would not release sufficient product for cleaning purpose. Therefore, it is a major challenge to ensure that there is no disintegration of the product during use, no wastage of product through mush generation yet the product is sufficiently soft to enable the users to pick up right quantity of product while cleaning dishes.
- 25 [0006] IN166806 discloses a process for manufacturing detergent bars for fabric washing having good strength and handling properties during transport and use by the incorporation of various dessicants during neutralisation. Fabric wash bars are generally not suitable for cleaning tough soil encountered on hard surfaces.
- [0007] It has now been found that dish wash bars can be formulated using alternative materials as binders in place of clays.
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Description of the Invention:

- [0008] Thus according to the invention there is provided a detergent bar composition essentially comprising;

- 10 to 20% by wt. of a detergent active ;
 40 3 to 25% by wt. of soluble alkali or alkaline earth metal sulphate 2 to 15% by wt of alkaline buffer salt 20 to 60% by wt. of a mixture of abrasive materials.

Detailed Description of the invention:**Detergent Actives:**

- [0009] The composition according to the invention will preferably comprise detergent actives, which are generally chosen from both anionic, nonionic, cationic, zwitterionic detergent actives or mixtures thereof. It is also possible to include low levels of soap in the formulation. It is specifically preferred to use anionic detergent actives.
- 50 [0010] Suitable anionic detergent active compounds are water soluble salts of organic sulphuric reaction products having in the molecular structure an alkyl radical containing from 8 to 22 carbon atoms, and a radical chosen from sulphononic acid or sulphuric acid ester radicals and mixtures thereof.
- [0011] Examples of suitable anionic detergents are sodium and potassium alcohol sulphates, especially those obtained by sulphating the higher alcohols produced by reducing the glycerides of tallow or coconut oil ; sodium and potassium alkyl benzene sulphonates such as those in which the alkyl group contains from 9 to 15 carbon atoms ; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow and coconut oil ; sodium coconut oil fatty acid monoglyceride sulphates ; sodium and potassium salts of sulphuric acid esters of the reaction product of one mole of a higher fatty alcohol and from 1 to 7 moles of ethylene oxide ; sodium and potassium
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salts of alkyl phenol ethylene oxide ether sulphate with from 1 to 8 units of ethylene oxide molecule and in which the alkyl radicals contain from 4 to 14 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralised with sodium hydroxide where, for example, the fatty acids are derived from coconut oil and mixtures thereof. The preferred water-soluble synthetic anionic detergent active compounds are the alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of higher alkyl benzene sulphonates and mixtures with olefin sulphonates and higher alkyl sulphates, and the higher fatty acid monoglyceride sulphates. The most preferred anionic detergent active compounds are higher alkyl aromatic sulphonates such as higher alkyl benzene sulphonates containing from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium salts of higher alkyl benzene sulphonates or of higher-alkyl toluene, xylene or phenol sulphonates, alkyl naphthalene sulphonates, ammonium diaminyl naphthalene sulphonate, and sodium dinonyl naphthalene sulphonate.

[0012] The term soap denotes salts of carboxylic fatty acids. The soap may be derived from any of the triglycerides conventionally used in soap manufacture consequently the carboxylate anions in the soap may contain from 8 to 22 carbon atoms.

[0013] Further examples of suitable detergent-active compounds are compounds commonly used as surface-active agents given in the well-known textbooks "Surface Active Agents", Volume I by Schwartz and Perry and "Surface Active Agents and Detergents", Volume II by Schwartz, Perry and Berch.

[0014] The total amount of detergent active compound to be employed in the detergent composition of the invention will preferably be from 10-20% by weight of the composition.

Sulphates:

[0015] The success of the invention lies in using soluble alkali or alkaline earth metal sulphates as a binders / builders for forming the formulation into a bar form in presence of abrasives and other conventional ingredients. The formulation also delivers the right hardness of the finished product while processing and hence facilitates direct on-line packing without needing any weathering as it is normally needed in conventional dishwash formulations.

[0016] The invention also allows the flexibility in processing sequence with regards to alkaline earth metal sulphates addition at pre and post neutralisation.

[0017] Suitable alkali and alkaline earth metal sulphates can be selected from sodium, magnesium, potassium, aluminium and calcium salt derivatives. These materials can be used individually or as a mixture.

Abrasives:

[0018] Suitable abrasives can be selected from, particulate zeolites, calcites, dolomites, feldspar, silicas, silicates, other carbonates, aluminas, bicarbonates, borates, sulphates and polymeric materials such as polyethylene. There can be an abrasive system with more than a single type of abrasive to achieve a balanced abrasive property. For eg. Studies show that combination of abrasives of different hardness in a formulation provide significant benefits in some of the user properties.

[0019] Preferred abrasives for use in general purpose compositions particularly bars have a Mohs hardness 2 - 6, one of the constraints for incorporation of abrasive material with higher hardness has been inability in development of a balanced formulation which can deliver increase level of abrasive properties without losing or any compromise on other user properties. Preferred average particle sizes for the abrasive fall in the range 25-400 microns, with values of 30-200 microns being preferred. Preferred levels of total abrasive soluble and insoluble together range from 20-60-wt % on product, more preferably in the range 40-60-wt%.

[0020] Besides mixtures of calcium and magnesium carbonates (dolomite) the essential abrasive component in the formulation the other most preferred abrasives are calcium carbonate (as Calcite), sodium hydrogen carbonate, potassium sulphate, zeolite, alumina, hydrated alumina, feldspar, talc and silica.

[0021] Calcite, feldspar and dolomite and mixtures thereof are particularly preferred due to their low cost, suitable hardness and colour.

Alkaline buffer salts:

[0022] The detergency builders / alkaline buffer salts used in the formulation are preferably inorganic and suitable builders include, for example, alkali metal aluminosilicates (zeolites), sodium carbonate, sodium tripolyphosphate (STPP), tetrasodium pyrophosphate (TSPP), and combinations of these. Builders / alkaline buffer salts are suitably used in an amount ranging from 2 to 15% by wt, preferably from 5 to 10% by wt.

Other Ingredients:

[0023] Other ingredients such as fillers, solvents, amines, perfumes, colouring agents, flourescers, enzymes can also be used in the formulation, for example, in an amount up to 10 wt%.

Fillers:

[0024] Fillers may be incorporated in the formulation if required and suitable for use in the formulation include kaolin, calcium carbonate (calcite), talc, soapstone, other clays and the combination of these materials, used singly or in combination, suitably in an amount ranging from 10 to 30% by weight.

[0025] The compositions according to the invention may optionally contain polymeric structuring agents to aid in providing appropriate rheological properties and in enhancing their distribution and adherence of the composition to the hard surface to be cleaned.

[0026] The invention will now be illustrated with respect to the following non-limiting examples.

Examples:

Example 1

Process of manufacture of control bars (Bar A):

[0027] A batch of 20 kg was processed by conventional bar processing technology. 3.5 kg of sodium carbonate and 7.0 kg of sodium sulphate was mixed with 5.85 kg of linear alkyl benzene sulphonic acid in a sigma mixer. This was followed by additions of water, 2.4 kg of STPP, 11.80 kg of inert filler (dolomite) and other minor ingredients were added and mixed. The mixing was continued and followed by extrusion, billeting and stamping.

Example 2

Process for making the bar according to the invention (Bar B):

[0028] A batch of 20 kg was processed by conventional bar processing technology. 2.7kg of sodium carbonate was mixed with 2.75 kg of linear alkyl benzene sulphonic acid in a sigma mixer. This was followed by additions of water, 4.0 kg of sodium sulphate, 10.0 kg of inert filler (dolomite) and other minor ingredients were added and mixed. The mixing was continued and followed by extrusion, billeting and stamping.

[0029] For ready reference the compositions of bars (A) and (B) are set out in Table 1.

Table 1

Composition %wt	Bar (A)	Bar (B)
LAS (Active detergent)	30	14
Sodium carbonate	12	11
Sodium sulphate	35	20
STPP	12	-
Fillers, other minor ingredients and water	11	55

[0030] The bars according to the invention and control were analysed for processing parameters such as hardness and in use properties such as mush, tough soil cleaning and bar integrity were studied using the following procedure.

Hardness

[0031] The extruded bar hardness is measured by cone type penetrometer at 0 'time and the same bar is monitored for 10 days. The measurements are taken by forcing a cone into a plane surface under a pressure created by the

addition of 50g for 5 seconds.

The Tough soil cleaning efficiency

- 5 [0032] The tough soil refers to burnt milk on stainless steel plates prepared using 2 ml of milk per plate at high temperature. The cleaning % is blind rated on visual & feel basis. The tests were carried out by trained expert panel members.

Mush

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- [0033] The tablets are placed in soap dishes dipped in 20 ml of water. The tablet bottom surface is observed visually for mush after 24 hrs.

Table 2

15	Test Parameter	Bar (A)	Bar (B)
	Processing	Very soft bars / Feathering observed (Fig 1)	Good bars
	Penetration at plodding	> 100	30
20	Day 2	80	13
	Day 3	70	12
	Day 4	60	12
	Day 8	55	12
25	Day 10	55	12
	Mush after water treatment	Very pasty loose mush (Fig.2)	Slight thick clingy mush
	Tablet shape retentivity after 24 hrs	Bottom grooves deformed (Fig. 2)	Bottom grooves retained
30	% Tough soil cleaning	30%	63%

- 35 [0034] The data presented in Table 2 shows that the bars according to the invention are processable to form good compact bars (Fig. 1) with sufficient hardness as compared to the Control. Even during use the bars retain their shape and superior integrity (Fig. 2). The bars are also superior to the control in its performance as hard surface cleaner which was estimated in terms of tough soil cleaning.

Claims

- 40 1. A detergent bar composition essentially comprising;
- 10 to 20% by wt. of a detergent active;
- 3 to 25% by wt. of soluble alkali or alkaline earth metal sulphate 2 to 15% by wt of alkaline buffer salt 20 to 60% by wt. of a mixture of abrasive materials.
- 45 2. A detergent bar according to claim 1 wherein the bar does not contain clay.

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 9350

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	DE 43 19 577 A (HENKEL KGAA) 15 December 1994 (1994-12-15) * claims 1-5 * * page 4, line 51 - page 5, line 15 * ---	1,2	C11D17/00 C11D3/14 C11D3/02 //C11D1/22, C11D3/10, C11D3/06
X	DE 36 40 541 A (HENKEL KGAA) 1 June 1988 (1988-06-01) * claims 1-6 * * page 3, line 15 - line 26 * ---	1,2	
X	GB 2 060 676 A (UNILEVER LTD) 7 May 1981 (1981-05-07) * claims 1-6; examples * * page 3, line 5 - line 24 * ---	1,2	
X	WO 98 38280 A (THE PROCTER & GAMBLE CO.) 3 September 1998 (1998-09-03) * examples I,II * ---	1,2	
X	WO 98 20103 A (PROCTER & GAMBLE) 14 May 1998 (1998-05-14) * claims; examples * ---	1,2	
D,A	DATABASE WPI Section Ch, Week 198825 Derwent Publications Ltd., London, GB; Class D25, AN 1988-168214 XP002135141 & BR 8 705 030 A (UNILEVER NV), 24 May 1988 (1988-05-24) * abstract * -----	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 May 2000	Examiner Serbetsoglou, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EP 99 30 9350 A1 (1999-03-03)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 9350

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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10-05-2000

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
DE 4319577	A	15-12-1994	NONE		
DE 3640541	A	01-06-1988	IN	169179 A	14-09-1991
			PH	25018 A	28-01-1991
GB 2060676	A	07-05-1981	BR	8006542 A	14-04-1981
			ES	495857 D	01-11-1982
			ES	8300849 A	01-02-1983
			GR	69992 A	23-07-1982
			IN	154772 A	15-12-1984
			KE	3564 A	01-11-1985
			MY	26086 A	31-12-1986
			OA	6623 A	31-08-1981
			PH	17712 A	19-11-1984
			PT	71899 A, B	01-11-1980
			AR	222908 A	30-06-1981
WO 9838280	A	03-09-1998	AU	1979097 A	18-09-1998
WO 9820103	A	14-05-1998	JP	11500489 T	12-01-1999
BR 8705030	A	24-05-1988	IN	166806 A	21-07-1990
			PH	23689 A	27-09-1989
			ZA	8707368 A	30-05-1989